

CLAIMS

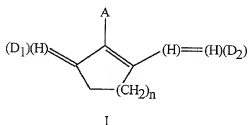
What is claimed is:

1. A near infrared sensitive composition, comprising:

(a) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the composition to undergo either

(i) effective photopolymerization or

(ii) effective photoimaging upon exposure to near infrared radiation, the near infrared dye is a compound of formula I:

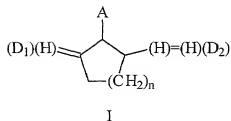


wherein substituent A is chosen from

- (1) a 5-6 membered heterocyclic ring system having 1-3 ring heteroatoms, in which the heteroatom is a nitrogen atom, which is substituted with a hydrogen atom,  $C_1-C_6$  alkyl,  $(CH_2)_mCO_2H$  or  $(CH_2)_mCO_2(C_1-C_6 \text{ alkyl})$  and the carbon atom of the heterocyclic ring system may be substituted with an oxygen atom to form a carbonyl or enolate anion and  $m$  is an integer ranging from 0-4;
- (2) a 5-6 membered carbocyclic moiety substituted with a hydrogen atom or a  $C_1-C_6$  alkyl group wherein a carbon atom of the alkyl group may be substituted with oxygen to form a carbonyl or enolate anion;
- (3) a quinoline or isoquinoline group wherein the nitrogen atom is directly bonded to the carbocyclic moiety of formula I;
- (4) N,N-bisaryl or bis( $C_1-C_6$  alkyl) or bisaryl( $C_1-C_6$  alkyl) amine wherein the aryl

- group is a naphthyl or phenyl group which is unsubstituted or substituted with a fluorine atom, bromine atom, chlorine atom,  $\text{OCH}_3$ ,  $\text{CF}_3$ ,  $\text{OH}$ , or  $\text{C}_1\text{-C}_6$  alkyl;
- 5 (5) a heterocyclic ring system having at least one nitrogen atom bonded directly to the carbocyclic ring of formula I and a group Z which is a carbon atom,  $\text{NR}^8$ , oxygen atom or sulfur atom wherein  $\text{R}^8$  is a hydrogen atom,  $\text{C}_1\text{-C}_6$  alkyl,  $\text{CO}_2\text{H}$  or  $\text{CO}_2\text{C}_1\text{-C}_6$  alkyl;
- 10 substituent  $\text{D}_1$  is a 9-15 membered heterocyclic system comprising a heteroaryl ring system having at least one heteroatom group (U) which is an  $\text{NR}^3$  group, oxygen atom, sulfur atom or  $\text{PR}^3$  group which is directly bonded to the aryl portion of the heteroaryl ring system and wherein  $\text{R}^3$  is a  $\text{C}_1\text{-C}_6$  alkyl which may be unsubstituted or substituted with  $\text{CO}_2\text{H}$ ,  $\text{SO}_3\text{H}$  or salts thereof and wherein the aryl ring may be unsubstituted or substituted with  $\text{OCH}_3$ ,  $\text{CF}_3$ , bromine atom, chlorine atom, fluorine atom,  $\text{C}_1\text{-C}_6$  alkyl or  $\text{OH}$  or a fused ring polycyclic heterocyclic system;
- 15 substituent  $\text{D}_2$  has the identical heterocyclic system as substituent  $\text{D}_1$  except that when U is  $\text{NR}^3$ , the nitrogen atom is quaternized to form an amine salt which is neutralized by an enolate anion from A when A is a substituted pyrimidine like moiety or by a discrete (non intra-molecular) anion;
- 20 n is an integer ranging from 1-2;
- (b) a hexaarylbiimidazole compound as photoinitiator;
- 30 (c) a photopolymerizable material and a chain transfer agent, or, instead of (c),
- (d) a photoimageable dye.
2. A photopolymerizable element comprising:
- (a) a support,
- 35 (b) a photopolymerizable composition comprising
- (i) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the photopolymerizable composition to

undergo effective photopolymerization upon exposure to near infrared radiation, the near infrared dye is a compound of formula I:



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wherein A is:

- (1) a 5-6 membered heterocyclic ring system having 1-3 ring heteroatoms, in which the heteroatom is a nitrogen atom which is substituted with a hydrogen atom,  $C_1-C_6$  alkyl,  $(CH_2)_mCO_2H$  or  $(CH_2)_mCO_2(C_1-C_6 \text{ alkyl})$  and the carbon atom of the heterocyclic ring system may be substituted with an oxygen atom to form a carbonyl or enolate anion and m is 0-4;
- (2) a 5-6 membered carbocyclic moiety substituted with hydrogen atom,  $C_1-C_6$  alkyl group wherein the carbon atom of the alkyl group may be substituted with oxygen to form a carbonyl or enolate anion;
- (3) quinoline or isoquinoline groups wherein the nitrogen atom is directly bonded to the carbocyclic moiety of formula I;
- (4) N,N-bisaryl or bis( $C_1-C_6$  alkyl) or bisaryl( $C_1-C_6$  alkyl) amine wherein the aryl group is a naphthyl or phenyl group which is unsubstituted or substituted with fluorine atom, bromine atom, chlorine atom,  $OCH_3$ ,  $CF_3$ , OH,  $C_1-C_6$  alkyl;
- (5) a heterocyclic ring system having at least one nitrogen atom bonded directly to the carbocyclic ring of formula I and a group Z which is a carbon atom,  $NR^8$ , oxygen atom, or sulfur atom wherein  $R^8$  is a hydrogen atom,  $C_1-C_6$  alkyl,  $CO_2H$  or  $CO_2C_1-C_6$  alkyl;

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substituent  $D_1$  is a 9-15 membered heterocyclic system comprising a heteroaryl ring having at least one heteroatom group (U) which is an  $NR^3$  group, oxygen atom, sulfur atom, or  $PR^3$  group which is directly bonded to the aryl portion of the heteroaryl ring system and wherein  $R^3$  is a  $C_1-C_6$  alkyl which may be unsubstituted or substituted with  $CO_2H$ ,  $SO_3H$  or salts thereof and wherein the

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aryl ring may be unsubstituted or substituted with  $\text{OCH}_3$ ,  $\text{CF}_3$ , bromine atom, chlorine atom, fluorine atom,  $\text{C}_1\text{-C}_6$  alkyl or OH or a fused ring polycyclic heterocyclic system;

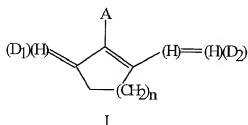
- 5 substituent  $\text{D}_2$  has the identical heterocyclic system as substituent  $\text{D}_1$  except that when U is  $\text{NR}_3$ , the nitrogen atom is quaternized to form an amine salt which is neutralized by an enolate anion from A when A is a substituted pyrimidine like moiety or by a discrete (non intra-molecular) anion;

n is an integer ranging from 1-2;

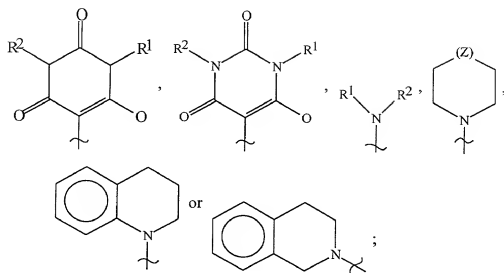
- 10 (c) a hexaarylbiimidazole compound as photoinitiator;  
(d) a photopolymerizable material and a chain transfer agent;  
and  
(e) a binder polymer.

3. A near infrared sensitive composition, comprising:

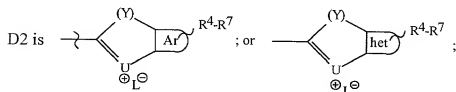
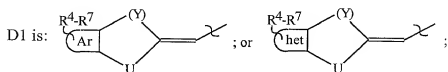
- 15 (a) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the composition to undergo either  
(i) effective photopolymerization or  
(ii) effective photoimaging upon exposure to near  
20 infrared radiation, the near infrared dye is a compound of formula I:



wherein substituent A is



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$R^1$  or  $R^2$  are independently selected from H,  $C_1$ - $C_6$  alkyl; or aryl wherein aryl is phenyl or naphthyl which may be unsubstituted or substituted with halogen,  $-O(C_1-C_6 \text{ alkyl})$ ,  $-O$ aryl, aryl or  $CF_3$ ; ( $C_1-C_6$  alkyl) ( $C_1-C_{10}$  aryl) or hydrogen;

is an aromatic ring chosen from phenyl or naphthyl;

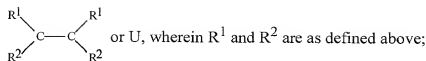
is a heteroaryl ring chosen from benzopyrazine, benzo-1,4-oxazine or benzo-1,4-thiazine.

U is selected from  $NR^3$ , S,  $PR^3$  or O;

Y is selected from  $C(R^1)(R^2)$ ;

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R<sup>3</sup> is selected from C<sub>1</sub>-C<sub>6</sub> alkyl unsubstituted or substituted with CO<sub>2</sub>H, SO<sub>3</sub>H or salts thereof;

R<sup>4</sup>-R<sup>7</sup> are independently chosen from H, OCH<sub>3</sub>, CF<sub>3</sub>, halogen;

Z is chosen from NR<sup>8</sup>, C, O or S;

R<sup>8</sup> is chosen from H, C<sub>1</sub>-C<sub>6</sub> alkyl, (CH<sub>2</sub>)<sub>m</sub>CO<sub>2</sub>H or (CH<sub>2</sub>)<sub>m</sub>CO<sub>2</sub>(C<sub>1</sub>-C<sub>6</sub> alkyl); and

m is 0-6;

n is 1-2;

provided that when A contains an enolate anion, a counterion L<sup>⊖</sup> is not present;

(b) a hexaarylbiimidazole compound as photoinitiator;

(c) a photopolymerizable material and a chain transfer agent; or, instead of (c),

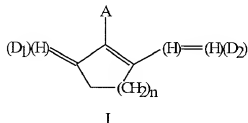
(d) a photoimageable dye.

4. A photopolymerizable element comprising:

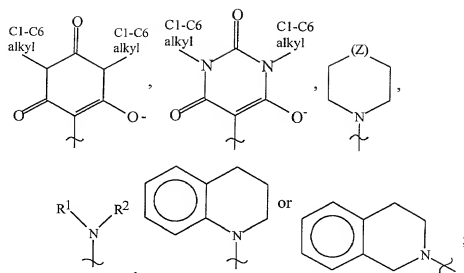
(a) a support;

(b) a photopolymerizable composition comprising

(i) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the photopolymerizable composition to undergo effective photopolymerization upon exposure to neared infrared radiation, the near infrared dye is a compound of formula I:

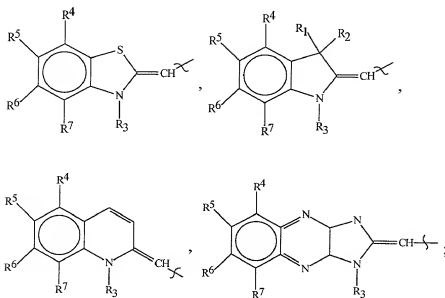


wherein A is



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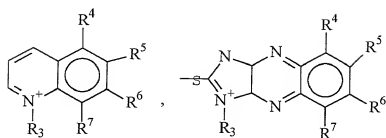
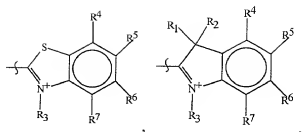
D<sub>1</sub> represents a heterocyclic ring structure selected from the group consisting of:



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D<sub>2</sub> represents a heterocyclic ring structure selected from the group consisting of

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- 5 R<sup>1</sup> or R<sup>2</sup> are independently selected from:

C<sub>1</sub>-C<sub>6</sub> alkyl, aryl wherein aryl is phenyl or naphthyl which may be unsubstituted or substituted with halogen, -O(C<sub>1</sub>-C<sub>6</sub> alkyl), Oaryl, aryl or CF<sub>3</sub>, (C<sub>1</sub>-C<sub>6</sub> alkyl) aryl or hydrogen;

- 10 R<sub>3</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> alkylsulfonate, C<sub>1</sub>-C<sub>6</sub> alkylloxycarbonyl, C<sub>1</sub>-C<sub>6</sub> alkyl, or C<sub>1</sub>-C<sub>6</sub> alkylcarboxy;

Z is selected from NR<sup>8</sup>, C, O or S wherein R<sup>8</sup> is H, C<sub>1</sub>-C<sub>6</sub> alkyl, CO<sub>2</sub>H or CO<sub>2</sub>(C<sub>1</sub>-C<sub>6</sub> alkyl);

- 15 R<sup>4</sup>-R<sup>7</sup> are independently selected from H, OCH<sub>3</sub>, CF<sub>3</sub>; or any two of R<sup>4</sup>-R<sup>7</sup> which when ortho substituents may join to form a phenyl ring; n is an integer ranging from 1-2 with the proviso that D<sub>2</sub> is selected to be the quaternized heterocyclic ring structure that corresponds to D<sub>1</sub> such that D<sub>1</sub> and D<sub>2</sub> together form a pair of heterocyclic ring structures;

- 20 (c) a hexaarylbiimidazole compound as photoinitiator;  
(d) a photopolymerizable material and a chain transfer agent; and  
(e) a binder polymer.

5. A near infrared sensitive composition, comprising:

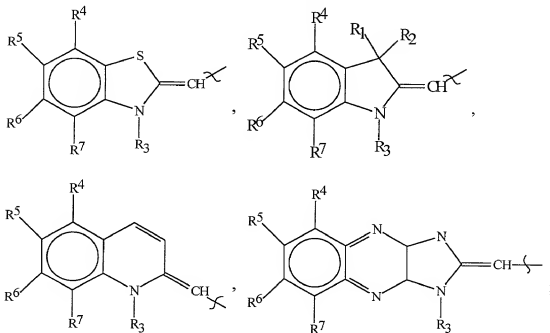
(a) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the composition to undergo either

- 25 (i) effective photopolymerization or  
(ii) effective photoimaging upon exposure

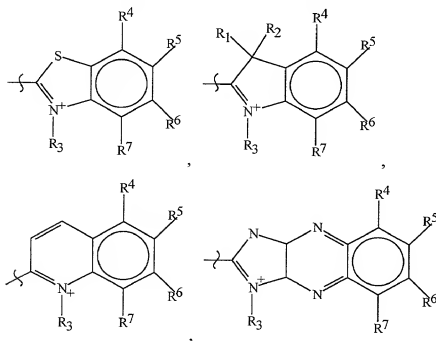




D<sub>1</sub> represents a heterocyclic ring structure selected from the group consisting of



D<sub>2</sub> represents a heterocyclic ring structure selected from the group consisting of



R<sub>1</sub> or R<sub>2</sub> are independently selected from:

C<sub>1</sub>-C<sub>6</sub> alkyl;

aryl wherein aryl is phenyl or naphthyl which may be unsubstituted or substituted with halogen, -O(C<sub>1</sub>-C<sub>6</sub> alkyl), Oaryl, aryl or phenyl, CF<sub>3</sub> (C<sub>1</sub>-C<sub>6</sub> alkyl)(C<sub>1</sub>-C<sub>10</sub> aryl) or hydrogen;

R<sub>3</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> alkylsulfonate, C<sub>1</sub>-C<sub>6</sub> alkyloxycarbonyl, C<sub>1</sub>-C<sub>6</sub> alkyl, or carboxy C<sub>1</sub>-C<sub>6</sub> alkyl;

Z is selected from NR<sup>8</sup>, C, O or S wherein R<sup>8</sup> is H, C<sub>1</sub>-C<sub>6</sub> alkyl, CO<sub>2</sub>H or CO<sub>2</sub>(C<sub>1</sub>-C<sub>6</sub> alkyl);

R<sup>4</sup>-R<sup>7</sup> are independently selected from H, OCH<sub>3</sub>, CF<sub>3</sub>; or any two of R<sup>4</sup>-R<sup>7</sup> which when ortho substituents may join to form a phenyl ring;

5 with the proviso that D<sub>2</sub> is selected to be the quaternized heterocyclic ring structure that corresponds to D<sub>1</sub> such that D<sub>1</sub> and D<sub>2</sub> together form a pair of heterocyclic ring structures.

7. The composition according to Claim 3, wherein the near infrared dye is selected from the group consisting of DF-1413, DF-1419, DF-1422, DF-1429,  
10 DF-1668, DF-12124, DF-15118, DF-15131, DF-15132, NK-3877, GW-826, GW-436, GW-776, GW-976, GW-186, and NK-2268; the hexaarylbiimidazole compound is selected from the group consisting of o-Cl-HABI, CDM-HABI, 2,3,5-TCI-HABI, and TCTM-HABI; wherein the photopolymerizable material is selected from the group consisting of tripropylene glycol diacrylate,  
15 trimethylolpropane triacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate, ethoxylated Bisphenol A dimethacrylate, and triethylene glycol dimethacrylate, and the chain transfer agent is selected from the group consisting of N-phenylglycine, julolidine, 2-mercaptobenzoxazole, 2,6-diisopropyl-N,N-dimethylaniline, and an organic  
20 thiol; or the photoimageable dye is selected from the group consisting of LCV, LECV, LPCV, LBCV, LV-1, LV-2 and LV-3.

8. The composition according to Claims 1, 2, 3 or 4 wherein the near infrared dye is present in at least 0.5% by weight of the total composition; the hexaarylbiimidazole compound is present in at least 0.5% by weight of the total  
25 composition; and the photopolymerizable material is present in at least 20% by weight of the total composition and the chain transfer agent is present in at least 0.1% by weight of the total composition; or the photoimageable dye is present in at least 0.5% by weight of the total composition.

9. The composition according to Claims 1, 2, 3, 4 or 5 which further  
30 comprises a binder polymer.

10. The composition according to Claims 1, 2, 3 or 4 wherein the composition, containing at least 0.5 weight percent of the near infrared dye, undergoes either (1) effective photopolymerization or (2) effective photoimaging  
35 to a photopolymerized or photoimaged photopolymer upon exposure to near infrared actinic radiation at a fluence of at least 100 mW/cm<sup>2</sup> (fluence units) for a period of at least 2 seconds (time units).